# Evidence for Insulating Behavior in the Electric Conduction of $(NH_3)K_3C_{60}$ Systems

H. Kitano[1], R. Matsuo[1], K. Miwa[1], A. Maeda[1], T. Takenobu[2,3], Y. Iwasa[2,3], T. Mitani[2]
[1]*Department of Basic Science, The University of Tokyo, Meguro-ku, Tokyo 153-8902, Japan*
[2]*Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa 923-1292, Japan*
[3]*Institute for Materials Research, Tohoku University, Aoba-ku, Sendai 980-8577, Japan*
(Dated:)

Microwave study using cavity perturbation technique revealed that the conductivity of antiferromagnet $(NH_3)K_{3-x}Rb_xC_{60}$ at 200K is already 3-4 orders of magnitude smaller than those of superconductors, $K_3C_{60}$ and $(NH_3)_xNaRb_2C_{60}$, and that the antiferromagnetic compounds are *insulators* below 250K without metal-insulator transitions. The striking difference in the magnitude of the conductivity between these materials strongly suggests that the Mott-Hubbard transition in the ammoniated alkali fullerides is driven by a reduction of lattice symmetry from face-centered-cubic to face-centered-orthorhombic, rather than by the magnetic ordering.

PACS numbers: 71.30.+h, 72.80.Rj, 74.70.Wz

The electronic and magnetic properties in $C_{60}$ are the subjects of renewed interest[1, 2]. In particular, the recent remarkable observations of high-temperature superconductivity (HTSC) in $C_{60}$ based field-effect transistors ($C_{60}$-FETs) [1] have attracted a lot of attention to non-cuprate HTSC. A critical temperature $T_c$ of 117 K for hole-doped $C_{60}/CHBr_3$ [1] seems to revive the possibility of exotic SC. On the other hand, remarkably, the BCS theory based on a band picture seems to work well even for the HTSC in $C_{60}$-FETs, since the simple relationship between $T_c$ and the effective volume $V$ per $C_{60}$, established in early studies on alkali($A$)-doped $C_{60}$ [3], still holds for the HTSC in $C_{60}$-FETs. Thus, the understanding of the mechanism for SC in $C_{60}$ systems is the subject of urgent importance in the condensed matter physics.

In close relation to this issue, recent studies on various alkali-doped fullerides strongly suggested the crucial roles of the electron-phonon (el-ph) and the electron-electron (el-el) interactions in $C_{60}$ systems. First, in contrast to band theory, $A_4C_{60}$ [4] and $Na_2C_{60}$ [5] have been reported to be nonmagnetic insulators, even though the latter material has a face-centered-cubic (fcc) structure that is isostructural to $A_3C_{60}$. Such a metal insulator transition (MIT) in $A_nC_{60}$ ($n$=2, 3, 4) may be understood in terms of a Jahn-Teller deformation of molecules [6, 7]. The second example is seen in $(NH_3)K_3C_{60}$ which is isovalent to $A_3C_{60}$ but showed no SC [8]. Due to the insertion of a neutral ammonia molecule, the crystal structure is face-centered-orthorhombic (fco). Recent experiments on $(NH_3)K_3C_{60}$ demonstrated that the ground state is an antiferromagnetic (AF) insulator, suggesting an aspect of the Mott-Hubbard (MH) system [9, 10, 11, 12].

The above two examples clearly indicate that the SC phase in $C_{60}$ systems competes with two kinds of insulating phases due to the strong el-ph and el-el interactions, suggesting the importance of both interactoins for the mechanism of HTSC. Thus, the full understanding of these instabilities in $C_{60}$ systems is crucially important.

However, to establish the MH picture in $(NH_3)K_3C_{60}$ systems, a crucial question is whether the paramagnetic phase above the Néel temperature, $T_N$, is metallic or not. This issue is quite controversial. Some experiments concluded that the MIT occurred at $T_N$ ($\sim$40 K) [10, 11], while others concluded that the high-temperature phase above $T_N$ was also insulating [12]. The main problem is that the previous experiments only investigated the magnetic properties of these materials [9, 10, 11, 12, 13]. There has been no study on the electric conduction of them. This is mainly because these materials are obtained only in the powder form at present, and because the ammonia content is easily affected in the pelletizing processes. Because of these difficulties, the dc resistivity and the optical reflectivity have not yet been measured. A further complication seems to arise from the orientational order transition of the K-$NH_3$ pairs at $T_S$(=150 K) [14].

In this paper, we report the first direct study of the electric conduction of $(NH_3)K_{3-x}Rb_xC_{60}$ ($x$=0, 2, 3) by using a microwave cavity perturbation technique. By comparing these results with our previous results from $K_3C_{60}$ and $(NH_3)_xNaRb_2C_{60}$ ($x$=0.8, 0.9) [15], and also with the results from other reference powders such as Pb, $V_2O_3$, and $C_{60}$, we concluded that the electric conduction of $(NH_3)K_{3-x}Rb_xC_{60}$ is *insulating* between 4.5 K and 250 K, without any MIT below 250 K. These results are in sharp contrast to the metallic nature of superconducting $(NH_3)_xNaRb_2C_{60}$ [15]. The striking difference between both materials strongly indicates that the Mott-Hubbard transition (MHT) in the ammoniated alkali fullerides is driven by a reduction of lattice symmetry from fcc to fco, rather than by the magnetic ordering.

The preparation of fco $(NH_3)K_{3-x}Rb_xC_{60}$ and fcc $(NH_3)_xNaRb_2C_{60}$ compounds has already been reported elsewhere [13, 16]. All sample powders were sealed in glass tubes under He. The average diameter of sample powders were estimated as 10$\pm$7 $\mu$m by the observation of the microscope image [15]. To measure the response for microwave magnetic ($H_\omega$) and electric ($E_\omega$) fields, we prepared a copper cylindrical cavity resonator operating at 10.7 GHz in the $TE_{011}$ mode, so one can choose the sample position between the antinode of the $H_\omega$-field and that of the $E_\omega$-field. The microwave loss $\Delta(1/2Q)$

and the frequency shift $\Delta f/f$ were measured between 4.5 K and 250 K. The response of the sample was obtained by subtracting the contribution of an empty tube with almost the same size as the sample tube. A set of careful measurements confirmed that the contribution of the glass tube to $\Delta(1/2Q)$ was very small, although the magnitude of $\Delta f/f$ was difficult to determine precisely. More details were described elsewhere [15].

Our idea to study the electric conduction of unknown powders is quite simple. $\Delta(1/2Q)$ and $\Delta f/f$ at $H_\omega$ (or $E_\omega$) are usually given as functions of the complex dielecric constant, $\epsilon(=\epsilon' + i\epsilon'')$, the complex magnetic susceptibility, $\chi(=\chi' + i\chi'')$, and the sample size $a$ [17]. In Fig. 1(a), we plot the calculated $\Delta(1/2Q)$ at $H_\omega$ and at $E_\omega$ [$\Delta(1/2Q)_H$ and $\Delta(1/2Q)_E$, respectively] as a function of the conductivity $\sigma(=\omega\epsilon''/4\pi)$ for several values of $a$ and $\epsilon'$. All data of $\Delta(1/2Q)$ are normalized by $\upsilon$, which is the volume ratio of the sample to the cavity. As shown in Fig. 1(a), we found that $\Delta(1/2Q)_H \gg \Delta(1/2Q)_E$ in the high conductive region ($\sigma \gtrsim 100\ \Omega^{-1}\mathrm{cm}^{-1}$), independent of $a$ and $\epsilon'$, while $\Delta(1/2Q)_H \ll \Delta(1/2Q)_E$ in the low conductive region ($\sigma \lesssim 0.1\ \Omega^{-1}\mathrm{cm}^{-1}$), for a nonmagnetic material ($\chi''\sim 0$). Thus, we can determine whether an unknown sample is conductive or not, only by comparing $\Delta(1/2Q)_H$ with $\Delta(1/2Q)_E$. Furthermore, as shown in Fig. 1(b), since $(\Delta f/f)_E$ increases with decreasing $\sigma$ we can determine the sign of $d\sigma/dT$ from the $T$ dependence of $(\Delta f/f)_E$, as discussed below.

For a magnetic insulator with a large $\chi''$, the situation is not so simple. As shown in Fig. 1(c), $\Delta(1/2Q)_H$ saturates with decreasing $\sigma$ when $\chi''$ is finite. In such a case, $\Delta(1/2Q)_H$ is dominated by $\chi''$, while $\Delta(1/2Q)_E$ depends on $\sigma$ and $\epsilon'$. Thus, $\Delta(1/2Q)_H$ and $\Delta(1/2Q)_E$ are expected to behave quite differently from each other.

Figure 2 shows $\Delta(1/2Q)_H$ and $\Delta(1/2Q)_E$ as functions of $T$, for several materials including $(NH_3)A_3C_{60}$. We also plot $(\Delta f/f)_E$ in the insets of the lower panels. First, we confirmed that $\Delta(1/2Q)_H \gg \Delta(1/2Q)_E$ for Pb, as a reference of metals, and that $\Delta(1/2Q)_H \ll \Delta(1/2Q)_E$ for $C_{60}$, as a reference of insulators, as shown in Figs. 2(a) and 2(f), respectively. We found that $\Delta(1/2Q)_H \gg \Delta(1/2Q)_E$ for $K_3C_{60}$ and $(NH_3)_{0.9}NaRb_2C_{60}$ from $T_c$ to 250 K. These results provide direct evidence for the metallic nature in $A_3C_{60}$ showing SC, even if $T_c$ is strongly reduced by the intercalation of $NH_3$.

We found that $\Delta(1/2Q)_H$ for Pb decreased with decreasing $T$, while that for $K_3C_{60}$ and $(NH_3)_xNaRb_2C_{60}$ increased with decreasing $T$, as shown in Figs. 2(a) to 2(c). However, such a behavior depends on $\sigma$ and $a$. Typical value of $\sigma$ is $\sim 10^3\ \Omega^{-1}\mathrm{cm}^{-1}$ for $K_3C_{60}$ ($T$=$T_c$) [3], and is $\sim 10^5\ \Omega^{-1}\mathrm{cm}^{-1}$ for Pb ($T$=77 K) [18]. On the other hand, the diameter of $K_3C_{60}$ powders was $\sim 10\ \mu$m [15], while that of Pb powders was 90$\sim$125 $\mu$m. Thus, $\Delta(1/2Q)_H$ for Pb (or $K_3C_{60}$) decreases (or increases) with increasing $\sigma$, as predicted in Fig. 1(a).

A quite different result was obtained for $(NH_3)K_3C_{60}$. As shown in Fig. 2(d) and its inset, the results of $(NH_3)K_3C_{60}$ indicated that $\Delta(1/2Q)_E \gg \Delta(1/2Q)_H$ between 4.5 K and 250 K, and that $(\Delta f/f)_E$ increased with decreasing $T$, which were quite similar to the case of $C_{60}$. These results strongly suggest that the electric conduction of $(NH_3)K_3C_{60}$ was *insulating* over the entire temperature range measured.

The result of $(NH_3)Rb_3C_{60}$ depicted in Fig. 2(e) was slightly different from that of $(NH_3)K_3C_{60}$. That is, $\Delta(1/2Q)_E \approx \Delta(1/2Q)_H$ between 4.5 K and 250 K, which is different from those of Pb and $C_{60}$. However, this does not mean that $\sigma$ of $(NH_3)Rb_3C_{60}$ is larger than that of $(NH_3)K_3C_{60}$. Since the behavior of $(\Delta f/f)_E$ of $(NH_3)Rb_3C_{60}$ was similar to that of $(NH_3)K_3C_{60}$ and

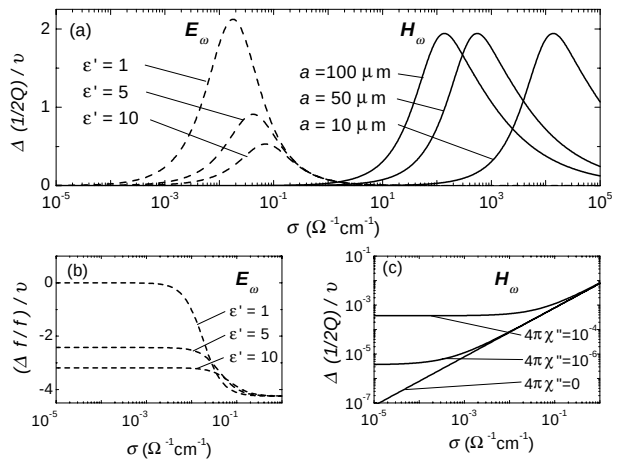


FIG. 1: (a) Calculated $\Delta(1/2Q)$ at $E_\omega$ and $H_\omega$ as functions of $\sigma$, for some values of $\epsilon'$ and $a$. Here, $\omega$ is $2\pi\times 10.7$ GHz. (b) Calculated $(\Delta f/f)_E$ for some values of $\epsilon'$. (c) $\Delta(1/2Q)_H$ for some values of $\chi$".

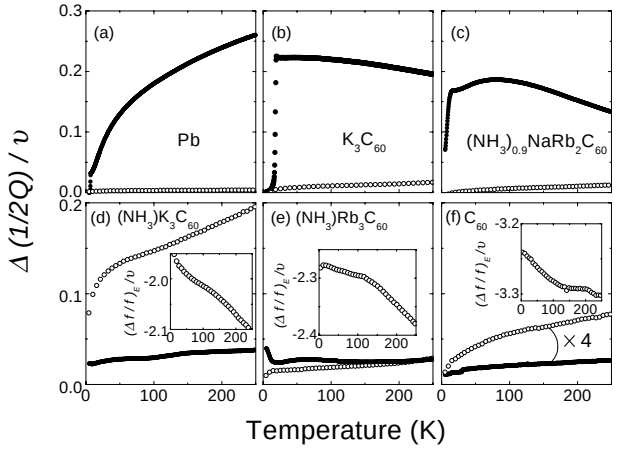


FIG. 2: The measured data of $\Delta(1/2Q)$ for (a) Pb, (b) $K_3C_{60}$, (c) $(NH_3)_{0.9}NaRb_2C_{60}$, (d) $(NH_3)K_3C_{60}$, (e) $(NH_3)Rb_3C_{60}$, and (f) $C_{60}$, respectively. Solid symbols are $\Delta(1/2Q)$ at $H_\omega$, and open symbols are $\Delta(1/2Q)$ at $E_\omega$. Insets: $(\Delta f/f)$ at $E_\omega$ for each material.

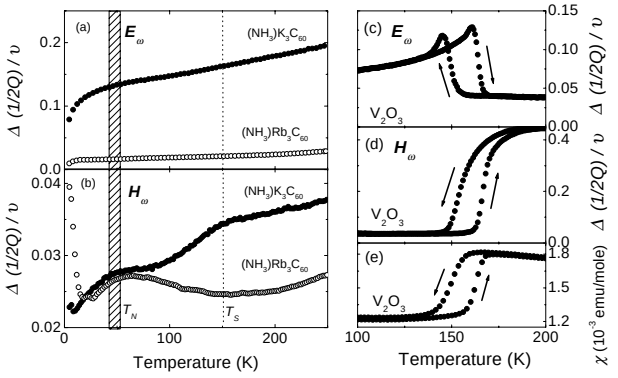


FIG. 3: (a) $\Delta(1/2Q)_E$ for $(NH_3)K_3C_{60}$ and $(NH_3)Rb_3C_{60}$. (b) $\Delta(1/2Q)_H$ for $(NH_3)K_3C_{60}$ and $(NH_3)Rb_3C_{60}$. (c) $\Delta(1/2Q)_E$ for $V_2O_3$. (d) $\Delta(1/2Q)_H$ for $V_2O_3$. (e) the dc magnetic susceptibility $\chi(T)$ of $V_2O_3$ The contribution of impurities was subtracted.

of $C_{60}$, it is suggested that $\sigma$ of $(NH_3)Rb_3C_{60}$ also decreased with decreasing $T$, and that it was located in a lower conductive region than the peak of $\Delta(1/2Q)_E$ in Fig. 1(a). Indeed, $\Delta(1/2Q)_E$ of $(NH_3)Rb_3C_{60}$ was found to be nearly an order of magnitude smaller than that of $(NH_3)K_3C_{60}$, while $\Delta(1/2Q)_H$ for both compounds were almost the same. We also found that the behavior of $\Delta(1/2Q)_E$ and $\Delta(1/2Q)_H$ were quite different from each other, as shown in Figs. 3(a) and 3(b). These features strongly suggest that $\Delta(1/2Q)_H$ of $(NH_3)K_3C_{60}$ and $(NH_3)Rb_3C_{60}$ were governed by $\chi''$ , as was already discussed. Thus, we conclude that $\sigma$ of $(NH_3)Rb_3C_{60}$ was also *insulating*, being smaller than that of $(NH_3)K_3C_{60}$.

Next, we discuss the controversial issue whether or not the MIT occurs in $(NH_3)K_3C_{60}$ systems with varing temperature. For this purpose, we also measured $V_2O_3$ powders. $V_2O_3$ is a typical Mott insulator which exhibits a MIT at $T_{\rm MI}$=150$\sim$160 K [19]. In Fig. 3, we compare the results of $(NH_3)K_{3-x}Rb_xC_{60}$ with those of $V_2O_3$. As shown in Figs. 3(c) and 3(d), we found that both $\Delta(1/2Q)_E$ and $\Delta(1/2Q)_H$ changed significantly at $T_{\rm MI}$. Here, $T_{\rm MI}$ was determined by measurement of the magnetic susceptibility using a dc SQUID magnetometer, independently, as shown in Fig. 3(e). Furthermore, we observed that $\Delta(1/2Q)_H \gg \Delta(1/2Q)_E$ above $T_{\rm MI}$ while $\Delta(1/2Q)_H \ll \Delta(1/2Q)_E$ below $T_{\rm MI}$, as was predicted in Fig. 1. These results indicate that both $\Delta(1/2Q)_E$ and $\Delta(1/2Q)_H$ are sensitive probes of the MIT. However, Figs. 3(a) and 3(b) show that $\Delta(1/2Q)_E$ varied very smoothly from 4.5 K to 250 K for both $(NH_3)K_3C_{60}$ and $(NH_3)Rb_3C_{60}$. Although $\Delta(1/2Q)_H$ of both compounds appeared to change slightly near $T_N$ or $T_S$, no anomaly was observed in $\Delta(1/2Q)_E$ at $T_N$ and $T_S$. Thus, we concluded that the MIT did not occur in $(NH_3)K_3C_{60}$ systems over the whole temperature range measured.

The above discussion based on $\Delta(1/2Q)$ and $\Delta f/f$ is straightforward but somewhat qualitative, and should be confirmed in terms of $\sigma$. We tried to estimate $\sigma$ as follows. First, the complex dielectric constant in the powder form, $\epsilon_p$, was obtained from $\Delta(1/2Q)$ and $\Delta f/f$ at $E_\omega$, by using the formula in the so-called "depolarization regime ", where the $E_\omega$-field almost uniformly penetrates into the sample [17].

$$\left(\frac{\Delta f}{f}\right)_E - i\Delta\left(\frac{1}{2Q}\right)_E = -\frac{\gamma}{n}\frac{\epsilon_p - 1}{\epsilon_p - 1 + \dfrac{1}{n}}, \qquad (1)$$

where $\gamma$ and $n$ is the geometrical factor ($\propto \upsilon$) and the depolarization factor (typically, $n\sim$0.4), respectively. Next, the effect of the powder form (porosity) was corrected by using the so-called Böttcher formula [20],

$$\frac{\epsilon - 1}{\epsilon + 2\epsilon_p} = \frac{1}{\delta}\frac{\epsilon_p - 1}{3\epsilon_p}, \qquad (2)$$

where $\delta$, $\epsilon$ are the packing fraction of the sample powder, and the complex dielectric constant of the bulk sample, respectively. We estimated $\delta$ as 0.2$\sim$0.25 for almost all samples, by comparing the apparent volume packed in the glass tube with the true volume estimated from the specific gravity [21]. Finally, $\sigma$ was obtained from $\epsilon''(=4\pi\sigma/\omega)$. In practice, the ambiguity in $\Delta f/f$ made the precise estimate of $\epsilon$ quite difficult. To avoid this difficulty, we utilized the fact that $\epsilon'_p$ depended on $\epsilon'$ only very weakly when $\delta$ was small. We found that $\epsilon'_p$ calculated by Eq. (2) was only varied from 1 to 2 for $\epsilon'$ ranged from 1 to 10. Thus, we assumed that $\epsilon'$ of $(NH_3)K_{3-x}Rb_xC_{60}$ was roughly 4$\sim$10 ($\epsilon'\sim$4 for $C_{60}$ [22]), and added a constant to $\Delta f/f$ so that $\epsilon'_p$=1$\sim$2.

Figure 4(a) shows $\sigma$ estimated at 200 K in this way for $(NH_3)K_{3-x}Rb_xC_{60}$ ($x$=0,2,3). In the same figure, we also plot our previous results for $K_3C_{60}$ and $(NH_3)_xNaRb_2C_{60}$ ($x$=0.8,0.9) [15]. We estimated the error bars for $\sigma$, considering the ambiguity of $\epsilon'(=4\sim10)$ and $\delta(=0.2\sim0.25)$ for $(NH_3)K_{3-x}Rb_xC_{60}$, and that of $a(=1\sim50\ \mu$m) for $K_3C_{60}$ and $(NH_3)_xNaRb_2C_{60}$. In spite of fairy large error bars, Fig. 4(a) clearly shows that $\sigma$ of $(NH_3)K_{3-x}Rb_xC_{60}$ is already at least 4 orders of magnitude smaller than the Mott limit for $C_{60}$ systems ($\sigma_{\rm Mott}$=500$\sim$700 $\Omega^{-1}$cm$^{-1}$)[23]. Thus, the results of Fig. 4(a) give quantitative support to our conclusion that $(NH_3)K_{3-x}Rb_xC_{60}$ is a genuine insulator.

When we compare these results with the previous results, our conclusion agrees with the recent NMR result by Tou *et al.* [12], but differs from the others [10, 11]. We found that a sample tube of $(NH_3)K_{3-x}Rb_xC_{60}$ including a small amount of the residual SC phase showed an apparent metallic behavior similar to $(NH_3)_xNaRb_2C_{60}$. One possible reason for the controversy may be such a non negligible contribution of the residual metallicity.

In Fig. 4(b), we plot $T_c$ and $V$, respectively. When we compare the results of Fig. 4(a) with 4(b), it is strongly suggested that the disappearance of SC is closely related to the drastic change in $\sigma$, implying the occurrence of MIT. This is most likely understood in terms of MHT, since the insulating phase was an antiferromagnet [9, 10, 11, 12, 13].

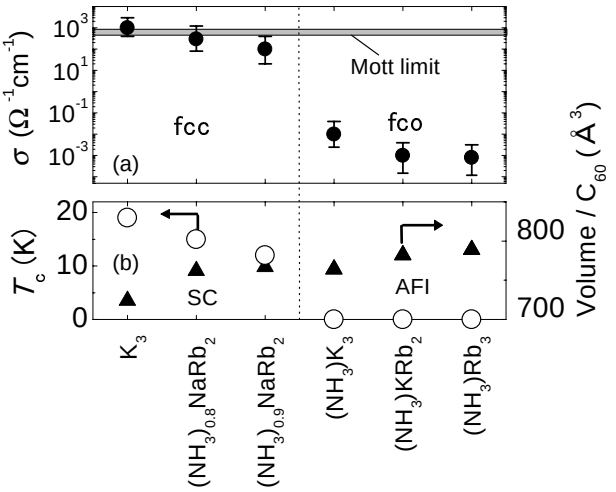


FIG. 4: (a) The estimated values of $\sigma$ at 200 K for $K_3C_{60}$, $(NH_3)_{0.8}NaRb_2C_{60}$, $(NH_3)_{0.9}NaRb_2C_{60}$, $(NH_3)K_3C_{60}$, $(NH_3)KRb_2C_{60}$, $(NH_3)Rb_3C_{60}$, respectively. (b) The plots of $T_c$ (open circle), and the volume $V$ per $C_{60}$ (solid triangle), respectively.

What is the origin of this MHT ? We must note that MHT does not occur with varing temperature, in contrast to the previous conclusion [10, 11]. As shown in Fig. 4(b), it is also unrelated to the change of $V$. We consider that the most probable candidate is a reduction of lattice symmetry from fcc to fco. A recent theoretical study [7] has suggested that the fcc structure of $A_3C_{60}$ favors the larger critical value $(U/W)_c$ for which the MHT occurs. Another possibility is that the less-symmetric configuration of $C_{60}$ removes the degeneracy of the $t_{1u}$ band, leading to a decrease of $(U/W)_c$ [3]. Such a MHT due to the lattice-symmetry reduction strongly suggests the significance of the highly symmetric configuration of $C_{60}$ for the bulk SC in $A_3C_{60}$.

Interestingly, in the cases of $C_{60}$-FETs [1], the lattice-symmetry reduction seems to be unimportant. Although the reason is unknown at present, such insensitivity of SC to the lattice symmetry may be related to the SC occuring only in a single layer of $C_{60}$ crystal. This deserves further investigation with prior importance.

In conclusion, we studied the electric conduction of $(NH_3)K_{3-x}Rb_xC_{60}$, by using the cavity perturbation technique. We confirmed that $(NH_3)K_{3-x}Rb_xC_{60}$ was insulating between 4.5 K and 250 K, without any MIT at $T_N$ and at $T_S$. We also found that $\sigma$ of $(NH_3)K_{3-x}Rb_xC_{60}$ at 200 K was already 3-4 orders of magnitude smaller than those of $K_3C_{60}$ and $(NH_3)_xNaRb_2C_{60}$. From the striking difference in $\sigma$ between these materials, we conjecture that the MHT in $A_3C_{60}$ systems is driven by the reduction of lattice symmetry from fcc to fco.

We thank T. Umetsu, R. Inoue, and H. Shimoda for experimental help, and D. G. Steel for a critical reading of the manuscript. This work was partly supported by the Grant-in-Aid for Scientific Research (10184101, 12046222, 13440110 and 13750005) from the Ministry of Education, Science, Sports and Culture of Japan.

[1] J. H. Schön *et al.*, Science **293**, 2432 (2001); J. H. Schön *et al.*, Nature **408**, 549 (2000); J. H. Schön *et al.*, Science **288**, 656 (2000).
[2] T. L. Makarova *et al.*, Nature **413**, 716 (2001).
[3] O. Gunnarsson, Rev. Mod. Phys., **69**, 575 (1997).
[4] For example, D. W. Murphy *et al.*, J. Phys. Chem. Solids **53**, 1321 (1992).
[5] V. Brouet *et al.*, Phys. Rev. Lett. **86**, 4680 (2001).
[6] S. Suzuki and K. Nakao, Phys. Rev. B **52**, 14206 (1995); M. Fabrizio and E. Tosatti, Phys. Rev. B **55**, 13465 (1997).
[7] J. E. Han *et al.*, Phys. Rev. Lett. **84**, 1276 (2000).
[8] M. J. Rosseinsky *et al.*, Nature **364**, 425 (1993).
[9] K. Prassides *et al.*, J. Am. Chem. Soc. **121**, 11227 (1999).
[10] Y. Iwasa *et al.*, Phys. Rev. B **53**, R8836 (1996).
[11] F. Simon *et al.*, Phys. Rev. B **61**, R3826 (2000).
[12] H. Tou *et al.*, Phys. Rev. B **62**, R775 (2000).
[13] T. Takenobu *et al.*, Phys. Rev. Lett. **85**, 381 (2000).
[14] K. Ishii *et al.*, Phys. Rev. B **59**, 3956 (1999); S. Margadonna *et al.*, Phys. Rev. B, **64**, 132414 (2001).
[15] A. Maeda *et al.*, Jpn. J. Appl. Phys. **39**, 6459 (2000); A. Maeda *et al.*, Physica C, **357-360**, 99 (2001).
[16] H. Shimoda *et al.*, Phys. Rev. B **54**, R15653 (1996).
[17] For example, O. Klein *et al.*, Int. J. Infrared and Millimeter Waves **12**, 2423 (1993).
[18] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt-Saunders, Philadelphia, 1976), pp. 8.
[19] A. Menth and J. P. Remeika, Phys. Rev. B **2**, 3756 (1970).
[20] C. J. F. Böttcher, *Theory of Electric Polarisation* (Elsevier, Amsterdam, 1952), pp. 415-420.
[21] H. Kitano *et al.*, in preparation.
[22] G. B. Alers *et al.*, Science **257**, 511 (1992).
[23] T. T. M. Palstra *et al.*, Phys. Rev. B **50**, 3462 (1994).